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**TECHNICAL OPERATIONS SUPPORT (TOPS) II
Delivery Order 0022: Research and Development of Advanced
Aerospace Coatings**

Universal Technology Corporation

**MARCH 2007
Final Report**

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MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
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*//Signature//

MARK N. GROFF, Project Manager
Thermal Sciences and Materials Branch
Nonmetallic Materials Division

//Signature//

KENNETH A. FEESER
Nonmetallic Materials Division
Materials and Manufacturing Directorate

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14. ABSTRACT The objective of this Delivery Order was to conduct basic research on development of novel materials for advanced aerospace coating applications. This research effort included development of quasi-crystal metallurgical and sol-gel coating materials for improved corrosion protections of aerospace aluminum alloys. Thorough testing and analysis of coatings structure and properties, investigation of mechanisms of their protection action, as well as understanding of structure-properties relationship for these materials was also included in this research effort, which covers the period from 25 September 2002 to 19 March 2007.					
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Introduction

The objective of this Delivery Order was to conduct basic research on development of novel materials for advanced aerospace coating applications. This research effort included development of quasi-crystal metallurgical and sol-gel coating materials for improved corrosion protection of aerospace aluminum alloys. Thorough testing and analysis of coatings structure and properties, investigation of mechanisms of their protection action, as well as understanding of structure-properties relationship for these materials was also included in this research effort, which covers the period from 25 September 2002 to 19 March 2007.

1. Research Activities

1.1 Development of nano-structured inorganic/organic hybrid coatings based on sol-gel processing of organo-functional silanes

The objective of this research task was to develop coating materials for long-term protection of the aerospace aluminum alloys against atmospheric corrosion and as an environmentally friendly alternative to existing chromate-based conversion coatings. For this purpose, inorganic/organic hybrid conversion surface coatings have been developed based on sol-gel processing of organo-functional silanes. We have continued development and improvement of the SNAP (Self-Assembled NAno-phase Particles) coating process, in which organo-silicate nano-particles with peripheral epoxy functional groups are pre-formed in an aqueous sol-gel process and then assembled and crosslinked upon application on the substrate surface. In summary, the developments of SNAP coating process included variations in crosslinking agents and in organic content of the sol-gel materials, the understanding of the process's solution chemistry and the improvements of coatings properties through incorporation of additional corrosion inhibitors.

The investigation of organo-functional silanes hydrolysis and condensation chemistry was performed experimentally by using a group of instrumental methods such as gel-permeation chromatography (GPC), X-ray diffraction (XRD), NMR, and Raman spectroscopy. In parallel to these studies, the coatings were deposited from solutions with variable chemistry at different "aging" time in the attempt to "freeze" the solution chemistry and to evaluate its effect on coating materials. We have found that it is important to allow some time (generally, 2-4 days) for solution reaction in the initial mixture of silanes. However, we found also that the content of epoxy-groups that are essential for second-stage crosslinking reactions and coating formation is slowly decreasing over time of solution aging. Thus, the optimum time for completion of the silane solution chemistry seemed to be within the range of 3-7 days for the formation of the best performing coatings.

In order to directly confirm the nanoparticle formation and self-assembling within the SNAP coating processing, we have attempted to investigate coating materials with the grazing-angle X-ray diffraction technique. The results of XRD confirmed the amorphous structure of the SNAP coatings with some arrangement on the order of nano-scale, which is comparable with the previous assumptions and the results of molecular modeling of the

nanoparticle formation process. Although, the XRD results demonstrated a certain degree of nano-scale ordering in the crosslinked films, the overall structure of SNAP materials is more likely dominated by the crosslinking chemistry rather than the mechanism of self-assembling of silica nano-particles.

The morphology and structure of the coatings was examined by Scanning Electron Microscopy (SEM) that was also used to determine the thickness of the coatings. We have performed extensive evaluation of coatings performance by the group of electrochemical methods and by the ASTM tests. Potentiodynamic scan (PDS) and electrochemical impedance spectroscopy (EIS) measurements were performed in dilute Harrison's solution (0.35 wt% $(\text{NH}_4)_2\text{SO}_4$ and 0.05 wt% NaCl, pH 5.5). The potentiodynamic polarization method was found very useful for rapid assessment of barrier properties of the coatings and for evaluation of the inhibitors' activity within the coating material. The method allowed accumulating such corrosion parameters as corrosion current density and corrosion potential, both associated with corrosion protection properties of the coating systems. The EIS technique was applied for long-term non-destructive monitoring of coatings' barrier properties upon immersion in corrosive electrolyte. The EIS data revealed that SNAP coating materials generally (if properly formulated) demonstrate exceptional stability of coating/substrate interface and are very resistant to corrosion, if coating is intact. In most cases, the EIS data were found well-correlated with visual inspection or with results of salt-spray testing.

Scanning vibrating electrode technique (SVET) measurements performed with the use of the SVET system of Applicable Electronics Inc. (Forestdale, MA, USA) allowed to monitor corrosion processes on micro-scale level suitable for monitoring galvanic corrosion associated with single copper-rich intermetallics of aluminum alloy 2024. This electrochemical technique was found to be especially suitable for corrosion monitoring within area of scribe for scribed coating samples. As a variation of an accelerated corrosion test, the special SVET technique was also developed, in which an artificial Al-Cu galvanic couple was made on the specimen surface by applying of a small amount of cupric chloride solution. This technique was very useful for evaluation of corrosion inhibitors and the coatings doped with inhibitors.

As non-chromated surface treatments for aluminum alloys, the conversion SNAP sol-gel coatings were incorporated into full coating systems, either fully non-chromated or partially non-chromated (with chromates present only in chromated primer). In order to compare corrosion protection performance against standard fully chromated coatings, we have performed vigorous testing of such coating systems using the following methods: ASTM B 117 Salt Spray, ASTM D 2803 Filiform Corrosion test, ASTM D 4541 Pull-off strength (PATTI) test, as well as electrochemical analysis of corrosion protection performance. It was concluded that in full coating systems sol-gel surface treatments still tend to underperform chromated coatings over long term exposure to corrosive electrolyte, though they demonstrate excellent adhesion and barrier properties, and are compatible with existing MIL-spec primers.

Sol-gel coatings with encapsulated organic corrosion inhibitors for corrosion protection of aluminum alloys.

Substantial amount of research work was devoted to development of sol-gel coatings with incorporated organic corrosion inhibitors.

The inclusion of corrosion inhibitors into barrier coatings is critical to improve corrosion protection performance, especially when coating's integrity is compromised by either mechanical damage (e.g. scratches, puncture holes, etc.) or inherent coating imperfections (air bubbles, micro-cracks, etc.). Under these conditions, the leachable inhibitor is able to diffuse out of the coating matrix to protect the exposed substrate against corrosion attack. The coating serves as protective barrier and as a reservoir for leachable corrosion inhibitor that is stored and released through the imbedded mechanism of reversible chemical interaction with the matrix material.

In this research project, we have shown that the hybrid sol-gel materials can be compatible with organic corrosion inhibitors, which can be incorporated into coating matrix through various mechanisms, such as physical entrapment within coating matrix, molecular encapsulation, or ion-exchange with ionizable functional groups of the coating material. We have proposed two different approaches for successful incorporation of organic corrosion inhibitors into coating matrix to achieve long-term and effective corrosion protection through a sustained release of inhibitor. These approaches are: a), the molecular incorporation of inhibitors as supramolecular complexes with cyclodextrin and b), reversible ion-exchange bonding of ionizable inhibitors with coating matrix material. The efficiency of active corrosion protection for these coating systems was examined by the group of electrochemical methods including potentiodynamic polarization (PDS), scanning vibrating electrode technique (SVET), electrochemical impedance spectroscopy (EIS), as well as by the ASTM methods (such as salt-spray and filiform corrosion resistance tests). The results of testing demonstrated both the effectiveness and limitations of these two approaches with the use of a number of selected organic inhibitors.

The results of the research on both these approaches for inhibitors incorporation have been discussed on multiple corrosion-related conferences and symposia and reported in several peer-reviewed journal publications. The invention disclose for the method of the inhibitors encapsulation was filed with the U.S. Patent and Trademark Office.

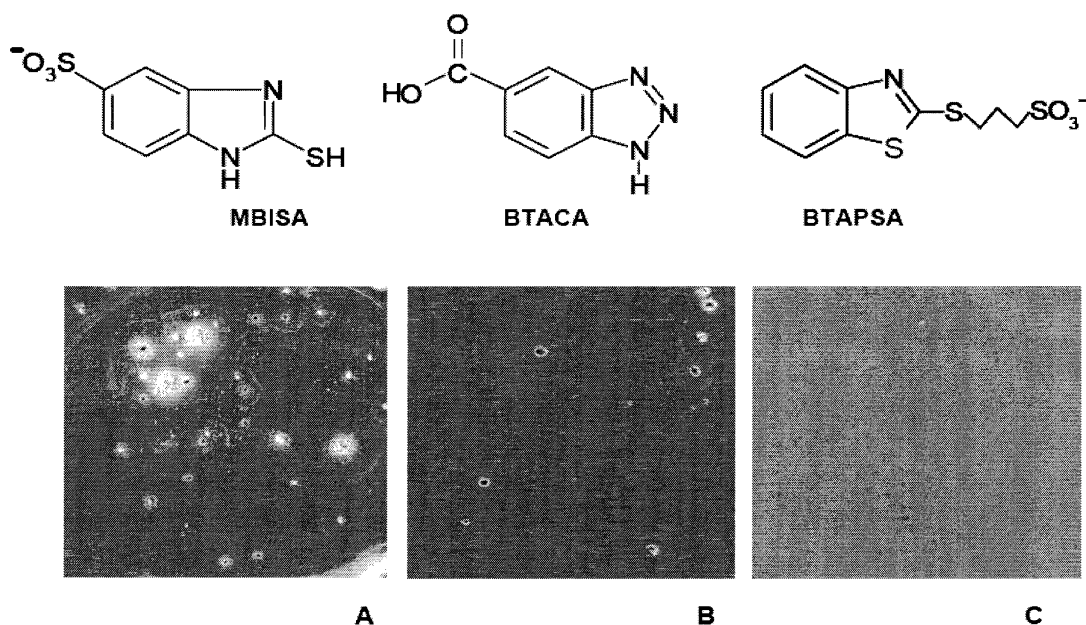


Fig. 1. Summary illustration on ionizable organic corrosion inhibitors:

Chemical structural formulas of studied corrosion inhibitors and the illustration of improvement in corrosion protection over control undoped system in very aggressive electrolyte solution: sol-gel coating samples with different loading of inhibitors after 1000 hrs of constant immersion in 5% NaCl solution: A – without inhibitor (control); B – with 0.25 M MBISA; C – with 0.25 M BTACA.

1.2 Quaternary Al-Transition Metal Quasicrystal-like Thin Films for Corrosion Protection of Aircraft Al Alloys (Task T-571)

Modification of Al substrates with quasicrystal films has shown great potential for corrosion protection of certain small parts of the aircraft (Fig. 1). Dr. Balbyshev and Dr. Khramov collaborated with Technology Assessment & Transfer on quasicrystal film coatings project as Part of Phase II of the SBIR.

Prior to each quasicrystal (qc) film sample being tested for corrosion protection by constant immersion EIS, it was thoroughly analyzed by EDS/SEM to obtain film thickness value, composition of the quasicrystalline material, and morphology of the film.

Top- and edge-view SEM analyses of quasicrystal films have shown that film composition and microstructure alone do not explain its superior resistance to electrolyte attack. Film morphology has been found to be an important factor contributing to the overall corrosion protection afforded by these coatings.

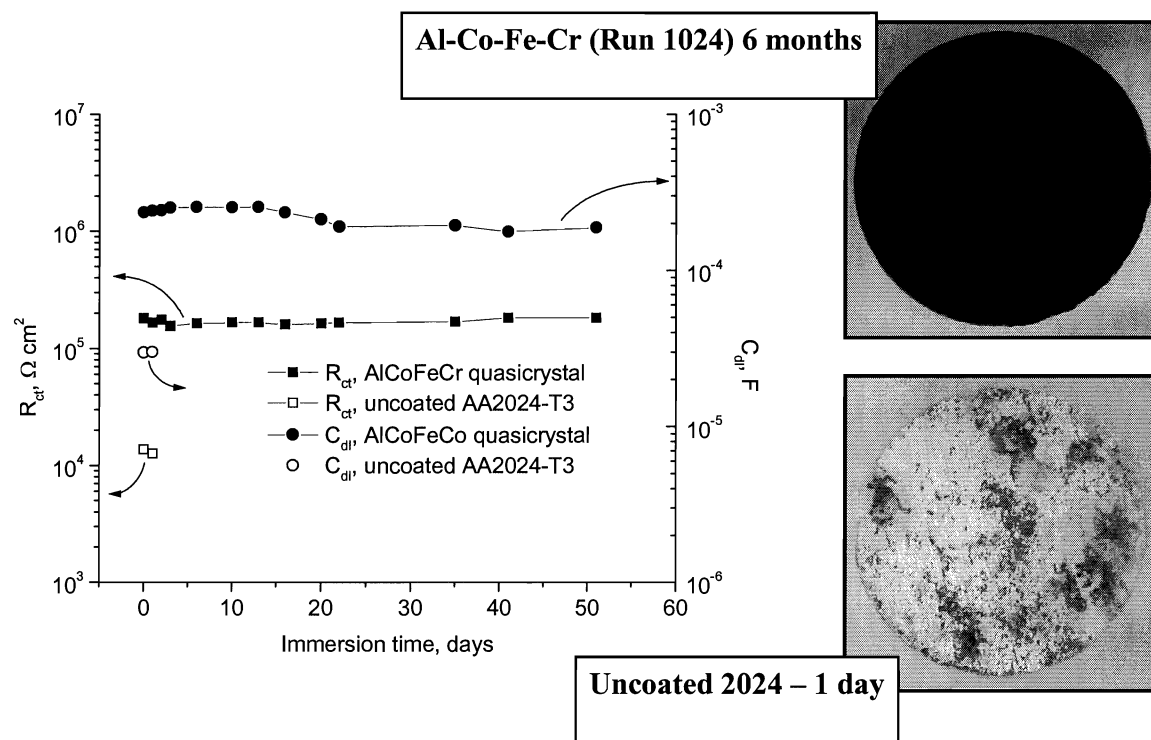


Figure 2. Previous studies (Phase I): Long-term electrochemical impedance spectroscopy on bare AA2024-T3 and coated with QC thin film (Run 1024).

Variable Film Thickness Studies. Several samples of qc-coated AA2024 were investigated by SEM: 1173 – 5 μm ; 1174 – 2 μm ; 1175 – 1 μm ; 1176 – 0.5 μm . All four coatings had dark gray appearance with no visible defects or film irregularities. Upon inspecting these films in edge-view SEM, we found that columnar structure was present in all four films (Fig. 2). More surface roughness was detected on the 0.5 μm film. It was also possible to estimate film thickness by SEM, and it was determined that film

thickness values for all 4 coatings were well within the specs ($\pm 15\%$). For the 5 μm film, column width was estimated $\sim 450\text{-}500\text{ nm}$.

Given the fact that all four films possess the same morphology, it is reasonable to expect similar electrochemical properties within this set of films. Any change in electrochemical behavior within the given set would most likely have to be due to the film thickness variation, and not caused by the structural characteristics of these films.

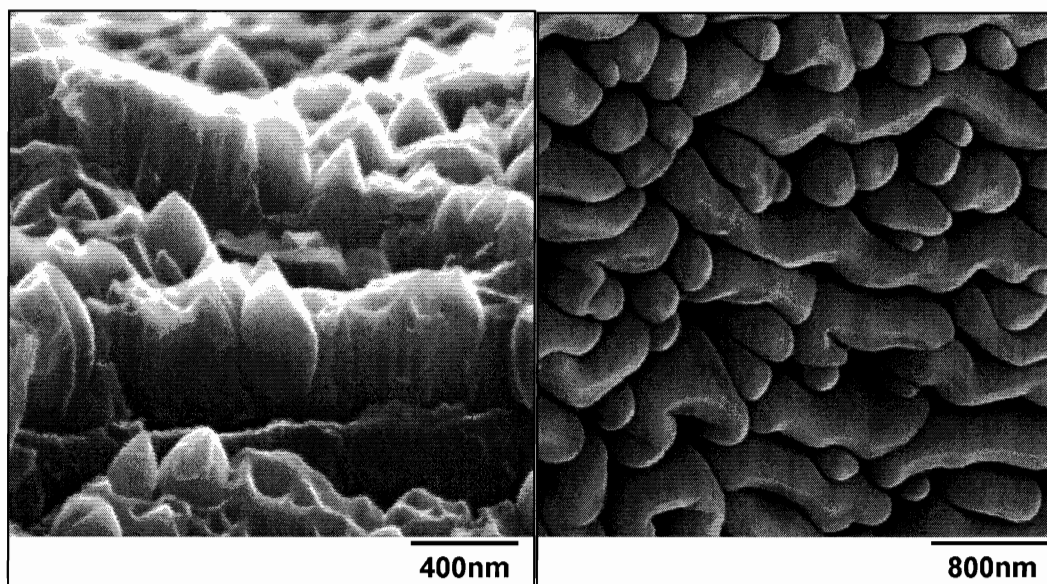


Figure 2. SEM micrographs of quasicrystal films. Film thickness: 0.5 μm (left) and 5 μm (right).

Electrochemical studies revealed that no signs of corrosion were visible on all but the 0.5 μm thick film throughout the 2 month immersion EIS test. The 0.5 μm film failed the immersion electrochemical impedance (EIS) test in dilute Harrison's solution (Fig. 3). Therefore, it was determined that the critical film thickness lies in the vicinity of 1 μm . Corrosion protection afforded by qc films is compromised below this value.

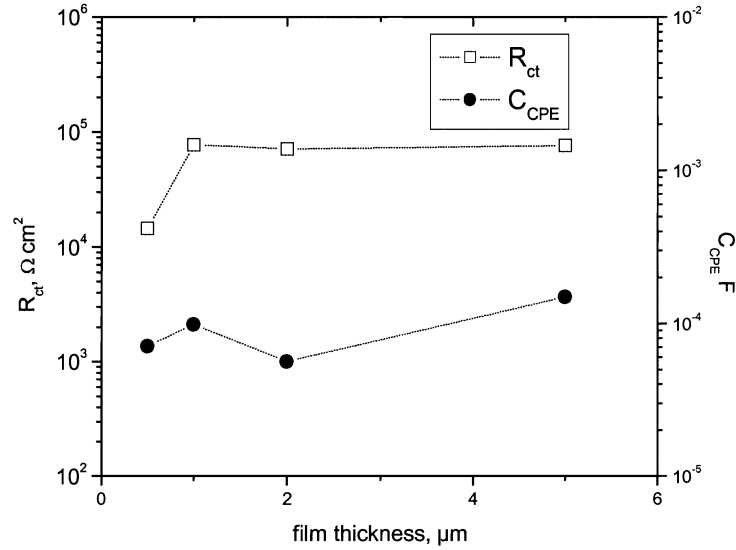


Figure 3. EIS equivalent circuit modeling parameters for various film thickness qc thin films. R_{ct} – charge transfer resistance, C_{CPE} – qc coating’s capacitance.

Effect of Variable Chloride Concentration. Varying the amount of chloride (Cl^-) in exposure electrolyte makes possible determination of an optimal range of applicability of these qc coatings. Qc thin films have shown to suppress corrosion of AA2024-T3 in dilute Harrison’s solution containing 0.05 wt.% NaCl and 0.35 wt.% $(\text{NH}_4)_2\text{SO}_4$. At the same time, these films fail constant immersion EIS test in more concentrated solutions, like 3.5% NaCl used in ASTM B117 corrosion test. For the purpose of this study we evaluated the corrosion performance of qc films by immersing them in solutions with various concentration of Cl^- ions, namely: 5%, 3%, 2%, 1%, 0.5%, and 0.05 %. We chose films with the nominal film thickness of 5 μm . The average film thickness was estimated by SEM and found to be well within specification: 5 $\mu\text{m} \pm 10\%$.

Using electrochemical impedance spectroscopy we determined that at chloride concentrations above 0.5%, qc thin films failed to protect the substrate from corrosion (Fig. 4) and showed visible signs of corrosion on the surface after 3 days of immersion in a chloride-containing solution.

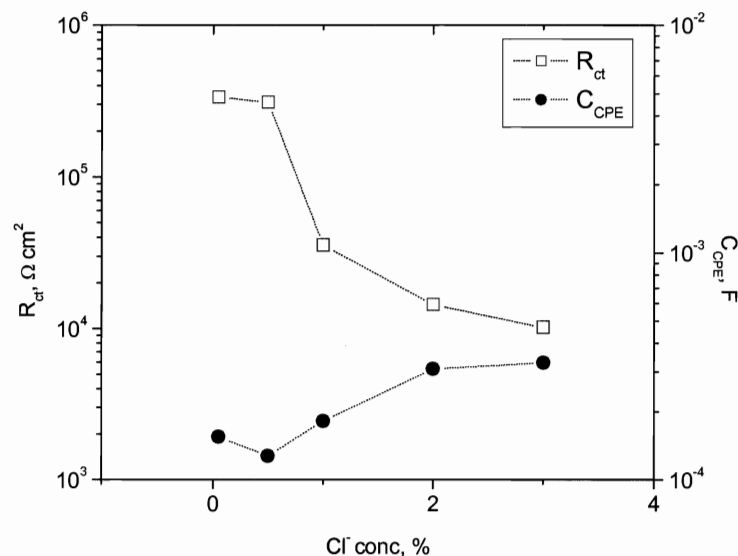


Figure 4. Immersion EIS parameters for qc films in chloride solutions of different concentration.

Annealing studies. The goal was to investigate the effect of annealing, its temperature and duration, on the corrosion protective properties of qc films.

Previously, it had been found that qc films annealed at 450°C for more than 1 hr or at 500°C for no longer than 1 hr develop cracks on the surface resulting in poor performance in corrosion tests. Phase I studies demonstrated that, upon annealing, the internal stress of the qc coating caused a sufficiently thin Al alloy panel to bow. Curled geometry of the panel made it unsuitable for corrosion tests. In Phase II studies the qc films were deposited on thicker Al substrates, which did not warp upon annealing. However, this time the qc coating itself cracked when the temperatures exceeded 450°C and when annealing was performed longer than 1 hr at 450°C. It was determined that annealing at 450°C for no longer than 1 hr did not cause structural degradation of the qc film (Figs 5, 6, and 7).

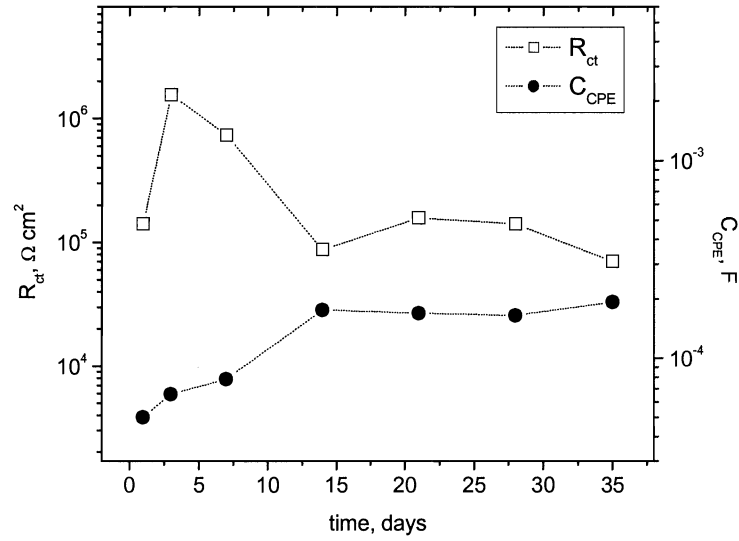


Figure 5. Effect of annealing on corrosion protection: 450°C for 2 hrs. Some micro-cracks observed on the surface prior to exposure, failure occurred within 2 weeks.

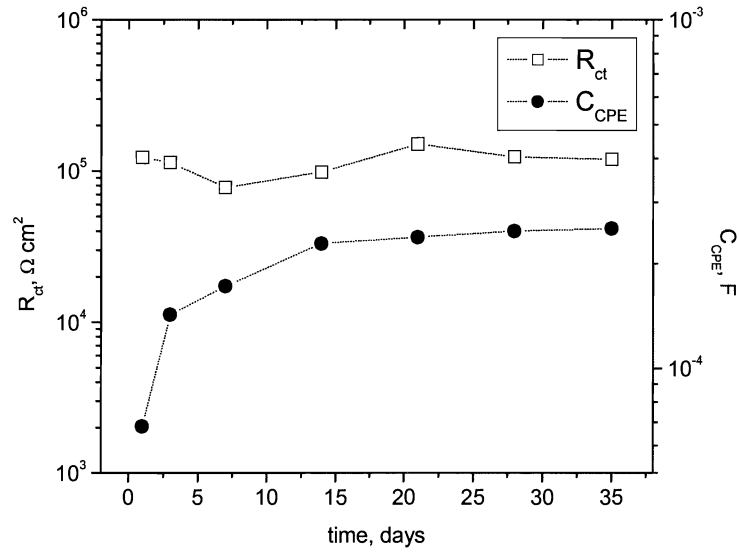


Figure 6. Effect of annealing on corrosion protection: 500°C for 1 hr. Corrosion product accumulation within 1 week of exposure.

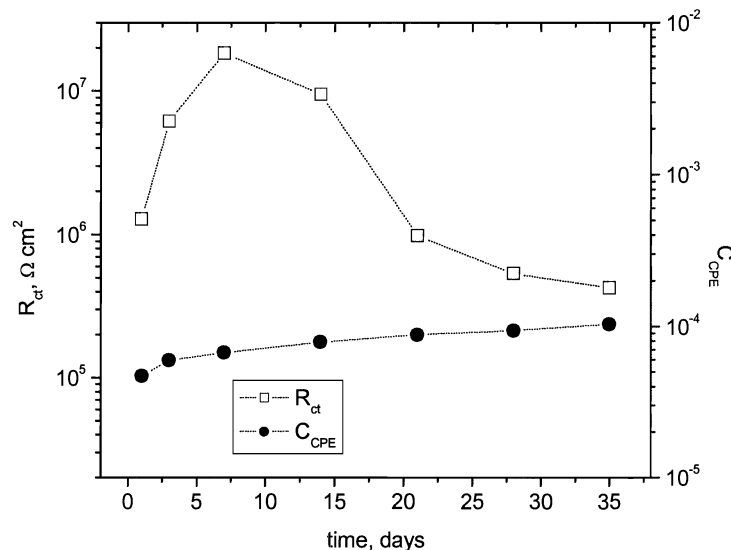


Figure 7. Effect of annealing on corrosion protection: 450°C for 1 hr. Improved corrosion protection through film densification; no visible signs of corrosion.

Hydrophobic modification. Aluminum-transition metal quasicrystal thin films have shown great potential in protecting Al alloys from corrosion in dilute, mildly acidic solutions. However, SEM imaging has shown these films to have porous, columnar structure. Upon immersion, corrosive electrolyte may fill these columns, thus significantly reducing the corrosion protection potential of the qc film. To prevent the ingress of electrolyte into the coating, an approach involving hydrophobic modification of qc thin film coatings was considered. The quasicrystal coatings were obtained from Technology Assessment & Transfer and treated in-house with a fluorocarbon-functional silane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)-triethoxysilane. Qc-like films with thickness values of 0.5 and 5 μm , as well as bare AA2024-T3 were dip-coated in the solution of the above silane in hexane in order to form a monolayer. The modified qc-like films and AA2024-T3 were studied by potentiostatic electrochemical impedance spectroscopy (EIS). EIS analysis revealed that hydrophobic modification of qc-like films failed to improve their corrosion protection properties and resulted in quick coating degradation upon immersion in dilute Harrison's solution (0.35% $\text{Na}(\text{SO}_4)_2$ and 0.05 % NaCl , pH=5.5). At the same time, hydrophobically-modified silane resulted in improved corrosion resistance of bare AA2024-T3. These findings bring us closer to the understanding of corrosion protection afforded by unmodified qc-like films and the underlying mechanism.

Corrosion Protection of Mg Alloys. Two Mg AZ31B coupons were coated with quasicrystalline material in order to investigate corrosion protection of Mg alloys afforded by quasicrystalline thin films. The qc-coated Mg has showed drastic improvement over the bare metal in terms of corrosion current and corrosion potential. The corrosion current (from PDS) decreased by almost 3 orders of magnitude, and the corrosion potential has shifted significantly in the more noble direction. EIS performance was marked by vast improvement over the uncoated Mg as well.

Film Hardness Studies. Apart from being able to afford good corrosion protection, quasicrystal films must also be mechanically durable. The hardness tests performed on the Nano-indenter were used to quantify the film's hardness. Most quasicrystalline films exhibited values between 80 and 100 GPa, but the value of 30 GPa was recorded for several films. The hardness test has proven to be a useful tool for further discrimination between qc films and correlation of their mechanical properties with structural characteristics.

Interrupted Growth Studies. SEM analysis of the previously studies qc films showed columnar structure, with columns oriented perpendicular to the substrate. This orientation in theory allows electrolyte to travel inside the column and eventually make contact with the substrate. TA&T utilized a slightly different magnetron sputtering procedure resulting in interrupted growth of quasicrystal films. While there is still no clear understanding of the mechanism of corrosion prevention by qc films, it is believed that if the column growth is interrupted, the ingress of electrolyte into the film will be minimized (Fig. 8).

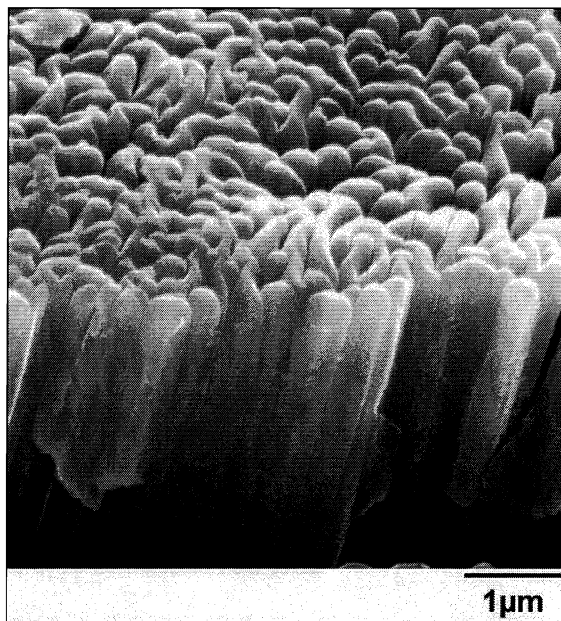


Figure 8. SEM micrograph of an “interrupted growth” quasicrystal thin film.

Contrary to the expected result, the structure appeared columnar in nature. Analysis of polarization curves (PDS) indicated a very low corrosion current, on the

order of tens of nanoamps. At the same time, EIS parameters did not change significantly during the first 7 days of constant immersion in dilute Harrison's solution. The film appeared to be retaining its barrier properties, as no corrosion products were visible on the surface exposed to electrolyte.

Selected Presentations

1. "Protection of Aluminum Alloys via Hybrid Sol-Gel Coatings with Encapsulated Organic Corrosion Inhibitors" A. N. Khramov, V. N. Balbyshev, and R. A. Mantz, presented at the 10th International Conference on Aluminum Alloys, July 9-13, 2006, Vancouver, Canada.
2. "Organo-Silicate Coatings with Phosphonate Functionalities for Corrosion Protection of Magnesium Alloys" A. N. Khramov, V. N. Balbyshev, L.S. Kasten and R. A. Mantz, presented at the International Conference on Metallurgical Coatings and Thin Films (ICMCTF 2005), May 2-6, 2005, San Diego, CA.
3. "Nanostructured Hybrid Organo-Silicate Coatings with Encapsulated Inhibitors for Active Corrosion Protection of Aluminum Alloys", A.N. Khramov, N.N. Voevodin, S. Balbyshev and R.A. Mantz, presented at the 2nd International Symposium on Aerospace Materials and Manufacturing: Development, Testing and Life Cycle Analysis, August 22-25, 2004, Hamilton, Ontario, Canada.
4. "Sol-Gel-Derived Corrosion-Protective Coatings with Controllable Release of Incorporated Organic Corrosion Inhibitors" A.N. Khramov, N.N. Voevodin, S. Balbyshev and M.S. Donley, presented at the International Conference on Metallurgical Coatings and Thin Films (ICMCTF 2004), April 19-23, 2004, San Diego, CA.
5. "Application of Inclusion Complexes of Cyclodextrin with Organic Corrosion Inhibitors for Corrosion Protection of Aluminum Alloys" A.N. Khramov, V.N. Balbyshev, N.N. Voevodin, and M.S. Donley, presented at the International Conference on Metallurgical Coatings and Thin Films (ICMCTF 2003), April 28-May 2, 2004, San Diego, CA.
6. "Hybrid Organo-Ceramic Corrosion Protection Coatings with Encapsulated Organic Corrosion Inhibitors", A.N. Khramov, V.N. Balbyshev, N.N. Voevodin, and M.S. Donley, presented at the 2003 Tri-Service Corrosion Conference, Las Vegas, NV, November 17-21, 2003.

Peer-reviewed publications

1. Khramov A.N., Balbyshev V.N., Kasten L.S. and Mantz R.A., Sol-Gel Coatings with Phosphonate Functionalities for Surface Modification of Magnesium Alloys, Thin Solid Films, 2006, 514, 174-181.

2. Khramov A. N., Balbyshev V. N., and Mantz R. A., Protection of Aluminum Alloys via Hybrid Sol-Gel Coatings with Encapsulated Organic Corrosion Inhibitors, Materials Science Forum, 2006, 519-521, 661-666.
3. N. Voevodin, D. Buhrmaster, J. Johnson, R. Mantz, V. Balbyshev, and A. Khramov, Nonchromated Coating Systems for Corrosion Protection of Aircraft Aluminum Alloys, Materials Performance, 2006, 45, 48-51.
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6. Khramov A.N., Voevodin N.N., Balbyshev V.N., and M.S. Donley, Hybrid Organo-Ceramic Corrosion Protection Coatings with Encapsulated Organic Corrosion Inhibitors, Thin Solid Films, 2004, 447-448, 549-557.
7. Balbyshev V.N., King D.J., Khramov A.N., Kasten L.S., and Donley M.S., Investigation of Quaternary Al-based Quasicrystal Thin Films for Corrosion Protection, Thin Solid Films, 2004, 447-448, 558-563.
8. Khramov A.N., Balbyshev V.N., Voevodin N.N., and Donley M.S., Nanostructured Sol-Gel Derived Conversion Coatings Based on Epoxy- and Amino-Silanes, Progress in Organic Coatings, 2003, 47, 207-213.
9. Balbyshev V.N., Khramov A.N., King D.J., Phillips B.S., Kasten L.S., and Donley M.S., Investigation of Nano-Structured Al-Based Quasicrystal Thin Films for Corrosion Protection, Progress in Organic Coatings, 2003, 47, 357-364.
10. Donley M.S., Balbyshev V.N., Mantz R.A., Khramov A.N., and Gaspar D.J., The Self-Assembled Nano-Phase Particle (SNAP) Process: A Nanoscience Approach to Coatings, Progress in Organic Coatings, 2003, 47, 401-415.

Patents and Patent Applications

1. Self-assembled Nano-Phase Particle Surface Treatment for Corrosion Protection, US 6,929,826 B1, Aug 16, 2005.
2. Phosphonate-modified sol-gel coatings with enhanced corrosion resistance on magnesium and magnesium alloys, Khramov A.N., Balbyshev V.N., Kasten L.S. and Mantz R.A.; Assigned AF Invention Number D 871

3. Method of metal corrosion protection by encapsulation of organic corrosion inhibitors within barrier coatings, Khramov A.N., Voevodin N.N., Balbyshev V.N., and Mantz R.A.; filed on 1/10/07 to the U.S. Patent and Trademark Office, assigned serial number 11/655,040